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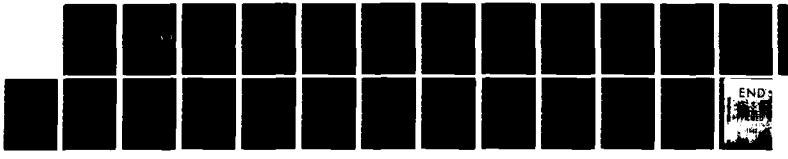

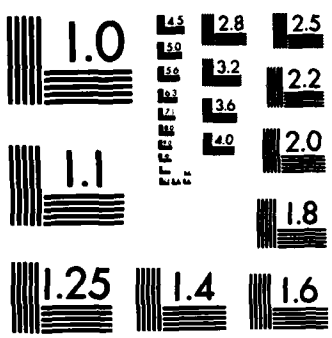

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COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES

Annual Progress Report

Harold L. Heller
Robert A. Erb, Ph.D.

AUGUST 1981

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The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. The projected systems are elastomeric-shelled, liquid-filled microcapsules. Improvements were made in the interfacial polymerization process, providing sealed capsules which do not inhibit the cure of matrix materials, and which do not harden with time. Further research is needed on larger-scale processing, on making smaller capsules, and on the mechanical properties of the capsules in matrices.

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ABSTRACT

The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. The projected composite systems are elastomeric-shelled, liquid-filled microcapsules. Experiments continued on the interfacial polymerization process, with spherical, sealed, capsules achieved. Diffusion of core liquid through the capsule walls has been reduced and the use of a tin catalyst has eliminated the cure inhibition of the matrix materials. Needs identified are better production methods, a reduction in capsule size and a catalyzed bath using a solvent other than kerosene.

FOREWORD

The concept behind this program is that a multiphase composite system should be able to simulate the mechanical properties of human soft tissue better than a homogeneous system could. The proposed composite of particular interest consists of liquid-filled, elastomeric-shelled microcapsules held together to form a deformable mass; this is to simulate the semi-liquid cellular structure of human soft tissue.

The fourth year's program has been directed toward the elimination of cure inhibition of the matrix elastomers, the elimination of the diffusion of core material through the urethane shells, and to some degree, the reduction of the capsule size. Cure-through over a period of time was a problem, and this has been eliminated by reducing the skin forming time in the bath to two minutes. Excellent quality, nearly transparent microcapsules can be made in small batches.

CONTENTS

FIGURES

1. INTRODUCTION

The soft tissues in maxillofacial areas have complex mechanical properties, and are difficult to replicate when preparing external facial prostheses. An area in particular in which further improvement is needed in facial prosthetics is in simulating the softness or "feel" of underlying soft tissues. This is particularly important if some movement capability is needed. The softest materials presently available are polymeric foams (which have the disadvantage of taking a permanent set by loss of gas when compressed) and gels (which are often unstable and sometimes lose internal liquid by syneresis).

This program is studying a new class of materials for use in fabricating maxillofacial prostheses: namely, liquid-filled, elastomeric-shelled microcapsules. Conceptually, such a product is attractive for several reasons: (1) the cells in the natural soft tissue are themselves composites of liquid (or semi-liquid) material in deformable shells; (2) the liquid-filled microcapsules could be stable entities free from the syneresis or gas-leakage of other soft materials; (3) the microcapsules could be stored as such and used by the prosthetist as an ultrasoft filler to modify other materials as needed.

In the first annual report the history of materials for maxillofacial prostheses was reviewed. Many materials have been used, but in recent times poly(vinyl chloride) plastisols, polyurethane compositions and silicones have been used effectively in simulation of skin and external features.

In the second annual report, efforts toward producing microcapsules by two experimental approaches were described. One approach involved coaxial extrusion of a catalyzed elastomer precursor and core liquid into a receiving bath. The other approach involved the interfacial polymerization of polyurethane around droplets of a core liquid suspended in a continuum containing reactive materials.

At the end of the second year, the coaxial extrusion approach was discontinued. The third annual report covers the further development of the

interfacial polymerization process to the point where microcapsules could be produced.

Work over the past year has included the successful switch to a tin catalyst to eliminate cure inhibition of the matrix polymers and defining the variables that affect the quality of the microcapsules.

2. DEVELOPMENT OF PRACTICAL TECHNIQUES FOR THE PREPARATION OF LIQUID-FILLED POLYURETHANE CAPSULESS

2.1 SUMMARY

An effective and flexible process has been developed for the preparation of liquid filled polyurethane capsules of the type believed to be suitable for use in preparation of polymer composite systems.

The new method utilizes a two-stage polymerization process in which a fragile polyurea skin is rapidly formed around a liquid droplet by interfacial polymerization as the first stage. After initial skin formation, a polyurethane wall membrane having the desired physical properties is formed by a slower, secondary process.

Capsules with strong, flexible wall membranes containing a variety of internal phases have been prepared by this method. The procedure appears to be readily adaptable to scaleup operations.

The urethane system selected for the capsule wall is of the cycloaliphatic diisocyanate type used to produce low modulus, light stable, elastomeric films. The liquid interior phase used at present for the maxillofacial prosthesis application is a non-reactive polypropylene glycol (Union Carbide Corp., PPG-2000).

Throughout most of this program, the core materials in the microcapsules had been found to slowly exude through the urethane walls. This problem had been overcome by using a higher molecular weight core material and reducing the curing time in the kerosene bath from over 20 minutes to two minutes.

Another problem solved in this year's work was the inhibition of the cure of matrix polymers from the presence of the amine catalyst used in the isocyanate/polyol reaction. This catalyst has been replaced with a tin catalyst which does not inhibit the cure of the matrix polymers.

In this report the present capsule forming system and the problems that have been encountered are described in detail.

2.2 TWO-STAGE DROP INTERFACIAL POLYMERIZATION SYSTEM

2.2.1 External (Continuous) Phase

Kerosene (Fisher, deodorized, 96 wt. %), 1,7 diaminoheptane (Aldrich D1740-8, 1 wt %), and fumed silica (Cabot Corp., Cab-O-Sil M-5, 3 wt %) are mixed with a high speed mixer to form a thickened exterior phase. The silica thickener is required to control the rate of fall of the liquid droplets through the exterior phase during the first stage of cure. The silica level is dependent on the viscosity of the droplet phase. 1,7-diaminoheptane reacts rapidly with the droplet to form a fragile "skin" which protects the capsule during the polyurethane formation.

2.2.2 Interior (Droplet) Phase

The interior phase consisted of:

(B-1) a cycloaliphatic diisocyanate
(B-2) a mixture of linear and chain-branched polyols capable of reacting with (B-1) to form a polyurethane
(B-3) a tin catalyst
(B-4) an inert polar liquid
(B-5) a trace of non-reactive dye (eosin) to facilitate identification of the beads.

B-1 - Isocyanate

The isocyanate presently used is methylene-bis-(4-cyclohexylisocyanate) (Desmodur W; Mobay). It is used in the manufacture of non-discoloring urethane. It is sensitive to water and humid air and must be stored under a blanket of dry nitrogen. The stannous octoate catalyst (B-3) is added to the isocyanate.

B-1 - Polyol Mixture

Pluracol P-2010, a Wyandotte diol (98.7 parts) and Pluracol PeP-450, a Wyandotte triol (1.3 parts) are mixed to form a reactive polyol phase capable of reaction with the isocyanate (B-1) to form a polyurethane. The polyol mixture (B-2) is added to the catalyzed isocyanate (B-1).

B-4 - Inert Polyol

The inert polyol core material presently used is polypropylene glycol (PPG-2000; Union Carbide). The eosin dye (B-5) is added to this polyol to improve the visibility of the microcapsules. The colored core material is added to the urethane (B-2 + B-1,3).

2.2.3 Interior (Droplet) Phase Formulation

The basic interior phase formulation presently used for microcapsule formation is as follows:

	%		
Isocyanate	99.8	72.7	50
Stannous octoate	0.2		
Pluracol PL-2010	98.7	27.3	
Pluracol PeP-450	1.3		
PPG-2000	100.0	-	50
Eosin	trace		

2.2.4 Preparation of Interior (Droplet) Phase

The catalyzed isocyanate is heated to 50°C and agitated by a magnetic stirrer. The polyol phase is added in a dropwise manner at approximately one drop per second. Since the isocyanate is sensitive to moisture the entire system is blanketed in dry nitrogen. The reaction appears to be nearly complete within an hour after the addition of the polyols, but the batch should not be used until the next day. The shelf life of this polyurethane is about 10 days, but it is best not to use it beyond five days.

The colored liquid core material is added to the polyurethane phase and thoroughly blended together. Due to the high viscosity of the urethane, air bubbles are trapped in the mixture and must be removed. This is accomplished by placing the batch in a vacuum for about 10 minutes. The bubble-free batch should not be used for several hours, but after this time, it is stable for at least four days.

2.2.5 Preparation of Polyurethane Capsules by Drop-Interfacial Polymerization

The freshly mixed external phase (A) is placed in an open vessel containing a suitably sized polypropylene mesh basket for collection and isolation of the capsules.

The internal phase is charged to a motor-driven syringe fitted with a suitable needle (a short 22 gauge needle was found to be suitable for many preparations, but other sizes can be used).

The internal phase is added dropwise to the curing bath with the needle tip approximately 4-8 cm above the bath surface. A variable speed turntable may be used to rotate the curing bath to provide a fresh surface for each droplet.

The droplets immediately form a fragile (polyurea) skin. They are allowed to remain in the curing bath for 2 to 3 minutes and then removed from the bath (via the mesh basket). They are rinsed in kerosene followed by a quick rinse in a dilute nonionic detergent solution (1% Triton X-100, Rohm and Haas Company). They are then removed from the basket, dried, and stored in a closed jar.

Figure 1 shows an example of the capsules made by the process mentioned above. Note that these capsules (shown at 2X) have nearly transparent shells, and that many have tails, some as long as twice their diameters. These tails do not present a problem in handling the capsules and should not interfere with the matrix polymers.

The tendency for tails to form is the result of the viscosity of the urethane increasing with age and/or dropping the drops from an insufficient height.

2.3 SYSTEM VARIABLES

2.3.1 Core Materials

The standard core material in the past year had been UCON fluid LB-385, a polyalkylene glycol. It had been noticed that fresh batches of the prepolymer

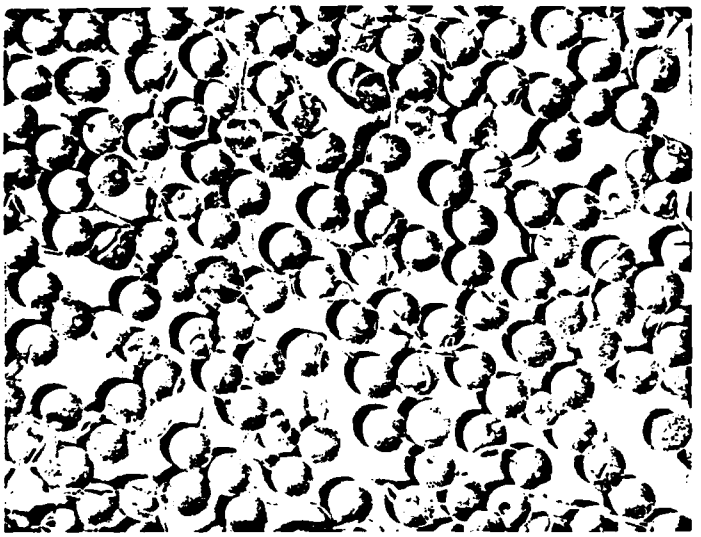

Figure 1. Polypropylene-Glycol Filled Microcapsules (2X)

Figure 2. Cut Cross Section of Microcapsules in MDX 4-4210 (12X)

and the LB-385 produced poor quality microcapsules, but after standing for several days, much better quality beads could be made. There appeared to be a delay in complete mixing which could be seen by the slow development of the eosin dye in the mix. On the other hand, the LB-385 is miscible with the kerosene and causes a weak seal at the top of the microcapsule.

In order to overcome the miscibility problems, polypropylene glycol (PPG) was evaluated as a core material. Using PPG, fresh batches could be used within several hours, and the weak point at the tail end of the capsules was eliminated. Although the bleeding out of the core material was greatly reduced with the two minute time limit in the bath, this problem still remained on long-term aging with the LB-385. A series of PPG liquids was evaluated using a range of moleculat weights from 425 to 2000. The degree of bleeding correlated well with the PPG molecular weight. The MW limit of 2000 gave the best results, but due to its high viscosity, larger drops are formed. Also, the rate of flow out of the needle must be carefully controlled, since higher rates produce an unbroken stream of the urethane going into the bath.

2.3.2 Batch Age

The prepared urethane batches are not stable and start to gel in about 7 days. Up until this time, they can be successfully used. There is a shorter shelf life for the urethane after the core material is added. Gelling does eventually occur, but the quality of the microcapsules is reduced by the seventh day of shelf life. As mentioned earlier, fresh batches need to be aged several hours before using.

2.3.3 Bath Thickeners

The kerosene bath is thickened with fumed silica to prevent the microcapsules from hitting the bottom of the container when they are dropped into it. HiSil 600 had been used in the past, but Cab-O-Sil M-5 is now used. The M-5 is clearer and disperses more readily in the solvent.

Now that a higher molecular weight core material is used, the droplets must be released from a greater distance above the bath to allow the tails to contract before passing through the surface. Four to eight centimeters above the bath is about ideal, and three percent Cab-O-Sil is about the ideal concentration. Higher concentrations were tried to eliminate the tails, but this caused irregular shell surfaces that had thin spots. The three percent level allows for some settling so that the drop initially comes in contact with the pure solution, forms a skin, and then comes to rest in the Cab-O-Sil layer.

2.3.4 Microcapsule Washing

After the microcapsules are removed from the bath, they must be washed, chiefly to get rid of the kerosene. They are first rinsed in clean kerosene to remove any Cab-O-Sil and remaining diaminoheptane. From this point, different methods have been used. The earlier approach was to quickly wash the microcapsules in an aqueous detergent solution followed by drying them on a paper towel.

Alcohol washing has been found to be unsatisfactory due to softening of the shells. The present technique used is to store the microcapsules in polypropylene glycol (PPG-425) after the kerosene rinse. The microcapsules are dumped out of the basket onto a paper towel to drain off excess kerosene, and then placed in the PPG for storage until the production run is finished. Storage in the PPG allows further curing without sticking together. This bath also removes any stray diaminoheptane by chemically reacting with it, forming a solid that is easily removed.

An interesting approach was tried for a continuous production technique which utilized a two layer bath. The lower layer consisted of PPG and the upper layer of slightly thickened kerosene containing diaminoheptane, and having a depth great enough to provide sufficient cure as the microcapsules pass through it. Unfortunately, the diaminoheptane gradually reacted with the PPG and formed a barrier at the interface.

The microcapsules can remain in the PPG for one day, but then should be removed and washed with water and dried for future use. Other solvents evaluated for washing include toluene and petroleum ether. Toluene is satisfactory and eliminates the need for a water wash. Petroleum ether, at this time, appears to be an excellent solvent wash.

2.3.5 Catalyzed Bath

The diaminoheptane appears to have a limited solubility in the kerosene, but up until recently, no problems were encountered from this. Recently it became time to produce larger batches of the microcapsules for composite testing, but it was found that the larger the single batches were produced, the poorer the quality of the microcapsules became, particularly in the shell elasticity.

This indicates that an insufficient amount of catalyst is available for a complete cure when a large number of droplets are released in the bath. This suggests the need for a solvent other than kerosene which itself has in the past been a problem.

Preliminary tests show that petroleum ether readily dissolves the diaminoheptane, thickens well with Cab-O-Sil and produces tough smaller diameter capsules than those formed in kerosene. The cure rate in the petroleum ether is so rapid, it is possible to remove the microcapsules from the bath within a half minute.

Petroleum ether evaporates rapidly and may cause some handling problems, which need to be considered.

3. REDUCTION IN MICROCAPSULE SIZE

By the present method of production, the capsule size is held nearly constant by the viscosity and capillarity effects that come into play when a drop falls free from the tip of the needle. The needle size has only a minor effect on the capsule size which is generally two millimeters in diameter.

Two air systems were tried for reducing the drop size. The first system was designed to produce jets of air around the flat tip of the needle to blow off small drops. The air was directed at the tip in a steep angle to force the drops away from the tip. This process did not blow off the liquid in small droplets, but removed the liquid in a spray mist.

The second approach tried was to inject the air into the liquid stream back inside the needle, but this too only removed the liquid in a spray mist.

From observing these processes, it was believed that the liquid drop must be completely out of the tube before it could be knocked away. Thus, by extending a tip down one side of the needle, it was thought that it might be possible to blow some of the liquid free from the free hanging drops. Again, this approach did not work.

One other approach tried was to disperse the urethane into small droplets in a liquid in which the urethane and core material are not soluble, and then dumping this mixture into the diaminoheptane bath. This approach has shown some success using silicone oil (Dow Corning 200) as the dispersing liquid. For a given batch, microcapsules in various sizes ranging from 0.3 to 1.5 mm in diameter were produced. These microcapsules cured through to solid beads in several days. It is possible that this method can be further improved, but at this time the variables affecting the quality of the microcapsules are best observed and controlled by the single drop production method.

4. COMPATIBILITY WITH CASTABLE ELASTOMERS

Up until this year, the microcapsules could not be used in bulk with castable elastomers due to the cure inhibition of the matrix elastomers by the amine curing agent used in forming the polyurethane. To avoid this problem we have switched to tin catalysts. Dimethyltin was found to be unsatisfactory due to its incompatiblity with the diaminoheptane. Stannous octoate was found to be ideal. In small quantities (0.2%) it provides a fast method for producing urethanes that do not inhibit the cure of the microcapsule shells.

Matrix elastomers of Dow Corning MDX 4-4210 Clean Grade Elastomer, Silastic 382 Medical Grade Elastomer and RTV 3145 can now be used without inhibition from the urethane catalyst. Figure 2 shows a cut cross section of capsules imbedded in MDX 4-4210.

5. MECHANICAL PROPERTIES

An improved testing device was built for measuring the mechanical properties of single capsules and capsule composites. The new device utilizes a piezoelectric crystal for measuring the load applied to a bead. This device has the advantage of being much more sensitive than the strain gauge system previously used. This system also as the advantage of an internal constant calibration, and it uses a non-bending platen. Furthermore, the platen is large enough to test cubes of capsule filled composite materials. The strain gauge arrangement previously used was operated at its maximum output which yielded a full scale readout of 400 grams. The piezoelectric device is used at an output level well under its full capacity. It was found that a full scale reading of 100 grams is about ideal for our present capsules.

The need for a better measurement technique resulted from our requirements to measure small changes in the compressive strength of the microcapsules as they age.

We are now able to calculate the forces applied to a single spherical capsule. All previous results were reported only as the applied load. The problems encountered with measuring the force per unit area was that the area of the contact surfaces of the capsules increased with increasing load. To overcome this problem, Dr. J. Stuart of Franklin Research Center (FRC) derived an equation for determining the radius of the contact surface for elastic spheres under compression. This equation is given below.

$$B = \left(\frac{1.33R}{d} - 0.013d^2\right)^{1/2} - 0.393d$$

where B is the radius of the contact surface, and:

R = the original radius of the sphere before compression
d = the distance between the compression plates.

An example of the results obtained by using the new compression rig and calculating the applied forces using the above equation is shown in Figure 3. The results obtained in this figure are averaged from five microcapsules taken from batch 149-9.

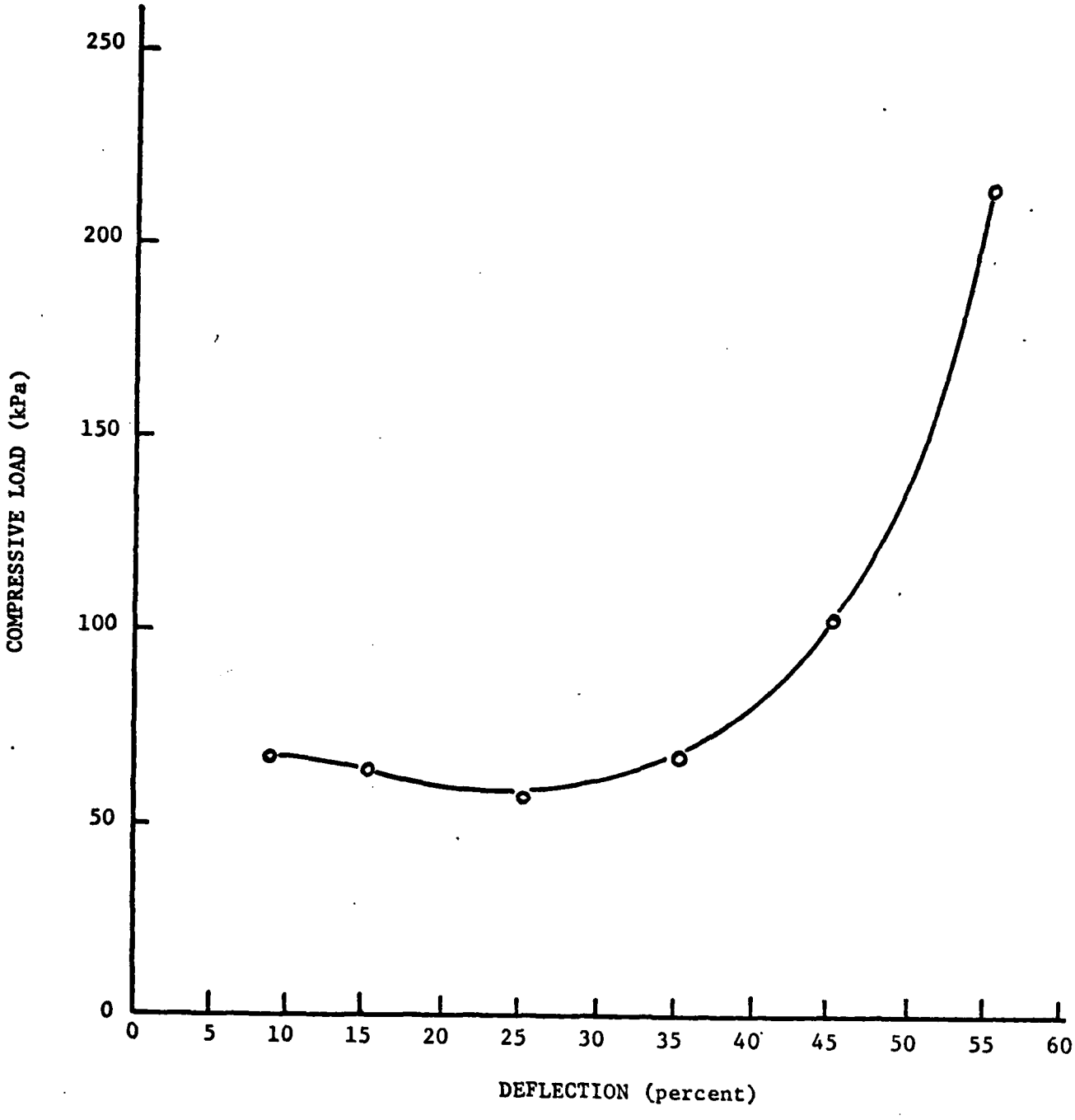

Figure 3. Compressive Properties of Urethane Microcapsules With Liquid Cores

Microcapsules from this batch have been tested over a two month period, starting with microcapsules only several hours old. Over this time period there appears to be no perceptible changes in softness and elasticity of the urethane shells.

6. FUTURE PLANS

The major problem encountered a year ago was the inability to define the variables that had an adverse effect on capsule quality. Now that these variables are much better understood and can be controlled, future work should advance significantly.

Four areas in which further work needs to be done are as follows:

1. Reduction in Microcapsule Size

To be used as a practical filler system, the diameter of the capsules should be substantially less than the thickness of the prosthetic structure to be fabricated. the present capsules, at about 2 mm in diameter, are too large for most applications. Efforts will be made to prepare capsules in diameters of 0.5mm and less. Approaches which will be considered are: using smaller diameter needles (than the present 22 gauge) for droplet formation, employing vibration techniques to produce smaller droplets, and dispersions in neutral liquids.

2. Advanced Production Methods

The present production method is ideal for making experimental batches, but not efficient enough to produce large quantities of the beads. We have not been working in this area, since the approach to be taken will depend somewhat on the method finally adopted for making the microcapsules. Three possible approaches include (1) multiple containers on a rotating table, (2) removal from the bath by a continuous belt, and (3) continuous bottom draining through a filter and recirculation of the liquid back into the top of the bath.

3. Improved Diaminoheptane Bath

The use of kerosene as the liquid portion of the bath has presented some problems with the rate of production and the permeability of the capsule shells. Other bath liquids such as petroleum ether will be evaluated.

4. Composites

It is now possible to produce composites without cure inhibition of the matrix polymer. The limiting factor now is the present production rate. With increased production, various composites will be made and mechanically tested.

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